

FORM PTO-1390 (Modified) (Rev. 11-2000)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		ATTORNEY'S DOCKET NUMBER <b>219667US</b>
<b>TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371</b>				U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR <b>10/049907</b>
INTERNATIONAL APPLICATION NO. <b>PCT/EP00/07704</b>	INTERNATIONAL FILING DATE <b>08 AUGUST 2000</b>	PRIORITY DATE CLAIMED <b>20 AUGUST 1999</b>		
<b>TITLE OF INVENTION</b> <b>PREPARATION OF A CRYSTALLINE, ZEOLITIC SOLID</b>				
<b>APPLICANT(S) FOR DO/EO/US</b> <b>Ulrich MUELLER, et al</b>				
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:				
<ol style="list-style-type: none"> <li><input checked="" type="checkbox"/> This is a <b>FIRST</b> submission of items concerning a filing under 35 U.S.C. 371.</li> <li><input type="checkbox"/> This is a <b>SECOND</b> or <b>SUBSEQUENT</b> submission of items concerning a filing under 35 U.S.C. 371.</li> <li><input checked="" type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (24) indicated below.</li> <li><input checked="" type="checkbox"/> The US has been elected by the expiration of 19 months from the priority date (Article 31).</li> <li><input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371 (c) (2))             <ol style="list-style-type: none"> <li><input type="checkbox"/> is attached hereto (required only if not communicated by the International Bureau).</li> <li><input checked="" type="checkbox"/> has been communicated by the International Bureau.</li> <li><input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US).</li> </ol> </li> <li><input checked="" type="checkbox"/> An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).             <ol style="list-style-type: none"> <li><input checked="" type="checkbox"/> is attached hereto.</li> <li><input type="checkbox"/> has been previously submitted under 35 U.S.C. 154(d)(4).</li> </ol> </li> <li><input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))             <ol style="list-style-type: none"> <li><input type="checkbox"/> are attached hereto (required only if not communicated by the International Bureau).</li> <li><input type="checkbox"/> have been communicated by the International Bureau.</li> <li><input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired.</li> <li><input checked="" type="checkbox"/> have not been made and will not be made.</li> </ol> </li> <li><input type="checkbox"/> An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).</li> <li><input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).</li> <li><input checked="" type="checkbox"/> An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).</li> <li><input type="checkbox"/> A copy of the International Preliminary Examination Report (PCT/IPEA/409).</li> <li><input checked="" type="checkbox"/> A copy of the International Search Report (PCT/ISA/210).</li> </ol>				
<b>Items 13 to 20 below concern document(s) or information included:</b> <ol style="list-style-type: none"> <li><input checked="" type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.</li> <li><input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.</li> <li><input checked="" type="checkbox"/> A <b>FIRST</b> preliminary amendment.</li> <li><input type="checkbox"/> A <b>SECOND</b> or <b>SUBSEQUENT</b> preliminary amendment.</li> <li><input type="checkbox"/> A substitute specification.</li> <li><input type="checkbox"/> A change of power of attorney and/or address letter.</li> <li><input type="checkbox"/> A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.</li> <li><input type="checkbox"/> A second copy of the published international application under 35 U.S.C. 154(d)(4).</li> <li><input type="checkbox"/> A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).</li> <li><input type="checkbox"/> Certificate of Mailing by Express Mail</li> <li><input checked="" type="checkbox"/> Other items or information: <b>Notice of Priority, PCT/IB/304/ PCT/IB/308 Amended Sheets 11 and 12 PTO Form-1449</b></li> </ol>				

U.S. APPLICATION NO. OR KNOWN <b>10/049907</b>		INTERNATIONAL APPLICATION NO. PCT/EP00/07704	ATTORNEY'S DOCKET NUMBER 219667US
24. The following fees are submitted:		<b>CALCULATIONS PTO USE ONLY</b>	
<b>BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :</b> <ul style="list-style-type: none"> <li><input type="checkbox"/> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO ..... \$1040.00</li> <li><input checked="" type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO ..... \$890.00</li> <li><input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO ..... \$740.00</li> <li><input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) ..... \$710.00</li> <li><input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) ..... \$100.00</li> </ul>			
<b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b>		<b>\$890.00</b>	
Surcharge of \$130.00 for furnishing the oath or declaration later than months from the earliest claimed priority date (37 CFR 1.492 (e)).		□ 20    □ 30	<b>\$0.00</b>
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE
Total claims	12 - 20 =	0	x \$18.00 <b>\$0.00</b>
Independent claims	2 - 3 =	0	x \$84.00 <b>\$0.00</b>
Multiple Dependent Claims (check if applicable).		<input type="checkbox"/>	<b>\$0.00</b>
<b>TOTAL OF ABOVE CALCULATIONS =</b>		<b>\$890.00</b>	
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27). The fees indicated above are reduced by 1/2.		<b>\$0.00</b>	
<b>SUBTOTAL =</b>		<b>\$890.00</b>	
Processing fee of \$130.00 for furnishing the English translation later than months from the earliest claimed priority date (37 CFR 1.492 (f)).		□ 20    □ 30	+ <b>\$0.00</b>
<b>TOTAL NATIONAL FEE =</b>		<b>\$890.00</b>	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable).		<input type="checkbox"/>	<b>\$0.00</b>
<b>TOTAL FEES ENCLOSED =</b>		<b>\$890.00</b>	
		Amount to be: refunded <b>\$</b> charged <b>\$</b>	
a. <input checked="" type="checkbox"/> A check in the amount of <b>\$890.00</b> to cover the above fees is enclosed.			
b. <input type="checkbox"/> Please charge my Deposit Account No. _____ in the amount of _____ to cover the above fees. A duplicate copy of this sheet is enclosed.			
c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <b>15-0030</b> . A duplicate copy of this sheet is enclosed.			
d. <input type="checkbox"/> Fees are to be charged to a credit card. <b>WARNING:</b> Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.			
NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.			
SEND ALL CORRESPONDENCE TO:			
703-413-3000 703-412-2220		Surinder Sachar Registration No. 34,423	
 <b>22850</b>		 <b>SIGNATURE</b> <b>Norman F. Oblon</b> <b>NAME</b> <b>24,618</b> <b>REGISTRATION NUMBER</b> <b>REB. 20 2002</b> <b>DATE</b>	

10/04/907

JC10 Recd PTO/USC 2.0 FEB 2002

Docket No. 219667US0PCT

IN RE APPLICATION OF: Ulrich MUELLER, et al.

SERIAL NO: New U.S. PCT Application based on PCT/EP00/07704

FILED: Herewith

FOR: PREPARATION OF A CRYSTALLINE, ZEOLITIC SOLID

ASSISTANT COMMISSIONER FOR PATENTS

WASHINGTON, D.C. 20231

SIR:

Transmitted herewith is an amendment in the above-identified application.

- No additional fee is required
- Small entity status of this application under 37 C.F.R. §1.9 and §1.27 is claimed.
- Additional documents filed herewith: English Translation, Declaration, Notice of Priority, Check for \$890.00, PCT Transmittal Letter, Preliminary Amendment, PCT/IB/304, PCT/IB/308, Information Disclosure Statement, Form PTO-1449, International Search Report, Translation of Annexes to the International Preliminary Examination Report Amended Sheets 11 and 12

The Fee has been calculated as shown below:

CLAIMS	CLAIMS REMAINING		HIGHEST NUMBER PREVIOUSLY PAID	NO. EXTRA CLAIMS	RATE	CALCULATIONS
TOTAL	12	MINUS	20	0	× \$18 =	\$0.00
INDEPENDENT	2	MINUS	3	0	× \$84 =	\$0.00
		<input type="checkbox"/> MULTIPLE DEPENDENT CLAIMS		+ \$280 =		\$0.00
					TOTAL OF ABOVE CALCULATIONS	\$0.00
		<input type="checkbox"/> Reduction by 50% for filing by Small Entity				\$0.00
		<input type="checkbox"/> Recordation of Assignment		+ \$40 =		\$0.00
					TOTAL	\$0.00

 A check in the amount of \_\_\_\_\_ is attached. Please charge any additional Fees for the papers being filed herewith and for which no check is enclosed herewith, or credit any overpayment to deposit Account No. 15-0030. A duplicate copy of this sheet is enclosed. If these papers are not considered timely filed by the Patent and Trademark Office, then a petition is hereby made under 37 C.F.R. §1.136, and any additional fees required under 37 C.F.R. §1.136 for any necessary extension of time may be charged to Deposit Account No. 15-0030. A duplicate copy of this sheet is enclosed.OBLON, SPIVAK, McCLELLAND,  
MAIER & NEUSTADT, P.C.\_\_\_\_\_  
Norman F. Oblon  
Registration No. 24,618

22850

Customer Number 22850

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(OSMMN 10/01)

Surider Sachar  
Registration No. 34,423

10/049907  
JC10 Rec'd PTO/PTO 2.0 FEB 2002

219667US-0PCT

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF :  
ULRICH MUELLER ET AL. :  
SERIAL NO: NEW U.S. PCT APPLN. : ATTN: APPLICATION BRANCH  
(Based on PCT/EP00/07704)  
FILED: HEREWITH :  
FOR: PREPARATION OF A CRYSTALLINE  
ZEOLITIC SOLID

PRELIMINARY AMENDMENT

ASSISTANT COMMISSIONER FOR PATENTS  
WASHINGTON, D.C. 20231

SIR:

Prior to examination on the merits, please amend the above-identified application as follows.

IN THE CLAIMS

Please amend the claims as shown on the marked-up copy following this amendment to read as follows.

3. (Amended) A process as claimed in claim 1, characterized in that the crystallization is carried out in the presence of at least one template compound.

5. (Amended) A process as claimed in claim 3, characterized in that template compounds which are included in the dried crystalline solid are separated from the solid by means of at least one wash process.

6. (Amended) A crystalline solid preparable by a process as claimed in claim 1, characterized in that the zeolitic material is a Ti, Ge, Te, Ta, V, Cr, Nb or Zr zeolite of the

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JULY 20 2004

structure type ABW, ACO, AEI, AEL, AEN, AET, AFG, AFI, AFN, AFO, AFR, AFS, AFT, AFX, AFY, AHT, ANA, APC, APD, AST, ATN, ATO, ATS, ATT, ATV, AWO, AWW, BEA, BIK, BOG, BPH, BRE, CAN, CAS, CFI, CGF, CGS, CHA, CHI, CLO, CON, CZP, DAC, DDR, DFO, DFT, DOH, DON, EAB, EDI, EMT, EPI, ERI, ESV, EUO, FAU, FER, GIS, GME, GOO, HEU, IFR, ISV, ITE, JBW, KFI, LAU, LEV, LIO, LOS, LOV, LTA, LTL, LTN, MAZ, MEI, MEL, MEP, MER, MFI, MFS, MON, MOR, MSO, MTF, MTN, MTT, MTW, MWW, NAT, NES, NON, OFF, OSI, PAR, PAU, PHI, RHO, RON, RSN, RTE, RTH, RUT, SAO, SAT, SBE, SBS, SBT, SFF, SGT, SOD, STF, STI, STT, TER, THO, TON, TSC, VET, VFI, VNI, VSV, WEI, WEN, YUG, ZON and ITQ-4 or of a mixed structure comprising two or more of these structures or a mixture of two or more of these zeolites.

8. (Amended) The use of a solid preparable as claimed in claim 1, or of a solid comprising at least one zeolitic material prepared by crystallizing from at least one precursor compound and the reaction discharge of the crystallization fed directly to a drying stage, drying being carried out in an atmosphere comprising less than 10% by volume of oxygen and at least one inert gas, characterized in that the zeolitic material is a Ti, Ge, Te, Ta, V, Cr, Nb or Zr zeolite of the structure type ABW, ACO, AEI, AEL, AEN, AET, AFG, AFI, AFN, AFO, AFR, AFS, AFT, AFX, AFY, AHT, ANA, APC, APD, AST, ATN, ATO, ATS, ATT, ATV, AWO, AWW, BEA, BIK, BOG, BPH, BRE, CAN, CAS, CFI, CGF, CGS, CHA, CHI, CLO, CON, CZP, DAC, DDR, DFO, DFT, DOH, DON, EAB, EDI, EMT, EPI, ERI, ESV, EUO, FAU, FER, GIS, GME, GOO, HEU, IFR, ISV, ITE, JBW, KFI, LAU, LEV, LIO, LOS, LOV, LTA, LTL, LTN, MAZ, MEI, MEL, MEP, MER, MFI, MFS, MON, MOR, MSO, MTF, MTN, MTT, MTW, MWW, NAT, NES, NON, OFF, OSI, PAR, PAU, PHI, RHO, RON, RSN, RTE, RTH, RUT, SAO, SAT, SBE, SBS, SBT, SFF, SGT, SOD, STF, STI, STT, TER, THO, TON, TSC, VET, VFI, VNI, VSV, WEI, WEN, YUG, ZON and ITQ-4 or of a

mixed structure comprising two or more of these structures or a mixture of two or more of these zeolites, and the zeolitic material comprises at least one element selected from the group consisting of aluminum, titanium, boron, iron, gallium, vanadium, zirconium, zinc, tin, tellerium, germanium, rare earth metals and a mixture of two or more thereof, and/or at least one element selected from the group consisting of sodium, potassium, magnesium, calcium, metals of groups Ib, IIb and VIIa and a mixture thereof, as a catalyst, as a support material for a catalyst, as a sorbent, as a pigment or as a filler for plastics.

Please add the following new claims.

10. (New) The process as claimed in claim 2, characterized in that the crystallization is carried out in the presence of at least one template compound.

11. (New) The process as claimed in claim 10, characterized in that, after contact with the atmosphere in the form of a carrier gas stream with the reaction discharge to be dried, condensable template compounds present in the stream are condensed out.

12. (New) The process as claimed in claim 11, characterized in that template compounds which are included in the dried crystalline solid are separated from the solid by means of at least one wash process.

REMARKS

Claims 3, 5-6 and 8 have been amended to remove multiple dependencies. Claims 10-12 are new claims. Support for the new claims is found in the original claims. An action on the merits and allowance of the claims is solicited. No new matter is added.

Respectfully submitted,

OBLON, SPIVAK, McCLELLAND,  
MAIER & NEUSTADT, P.C.



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<b>Marked-Up Copy</b>
Serial No.:
Amendment Filed on:
<u>2-20-2002</u>

IN THE CLAIMS

Please amend the claims as follows.

--3. (Amended) A process as claimed in [any of claims 1 and 2] claim 1,

characterized in that the crystallization is carried out in the presence of at least one template compound.

5. (Amended) A process as claimed in claim 3 [or 4], characterized in that template compounds which are included in the dried crystalline solid are separated from the solid by means of at least one wash process.

6. (Amended) A crystalline solid preparable by a process as claimed in [any of claims 1 to 6] claim 1, characterized in that the zeolitic material is a Ti, Ge, Te, Ta, V, Cr, Nb or Zr zeolite of the structure type ABW, ACO, AEI, AEL, AEN, AET, AFG, AFI, AFN, AFO, AFR, AFS, AFT, AFX, AFY, AHT, ANA, APC, APD, AST, ATN, ATO, ATS, ATT, ATV, AWO, AWW, BEA, BIK, BOG, BPH, BRE, CAN, CAS, CFI, CGF, CGS, CHA, CHI, CLO, CON, CZP, DAC, DDR, DFO, DFT, DOH, DON, EAB, EDI, EMT, EPI, ERI, ESV, EUO, FAU, FER, GIS, GME, GOO, HEU, IFR, ISV, ITE, JBW, KFI, LAU, LEV, LIO, LOS, LOV, LTA, LTL, LTN, MAZ, MEI, MEL, MEP, MER, MFI, MFS, MON, MOR, MSO, MTF, MTN, MTT, MTW, MWW, NAT, NES, NON, OFF, OSI, PAR, PAU, PHI, RHO, RON, RSN, RTE, RTH, RUT, SAO, SAT, SBE, SBS, SBT, SFF, SGT, SOD, STF, STI, STT, TER, THO, TON, TSC, VET, VFI, VNI, VSV, WEI, WEN, YUG, ZON and ITQ-4 or of a

mixed structure comprising two or more of these structures or a mixture of two or more of these zeolites.

8. (Amended) The use of a solid preparable as claimed in [any of claims 1 to 5] claim 1, or of a solid [as claimed in claim 7 or 8] comprising at least one zeolitic material prepared by crystallizing from at least one precursor compound and the reaction discharge of the crystallization fed directly to a drying stage, drying being carried out in an atmosphere comprising less than 10% by volume of oxygen and at least one inert gas, characterized in that the zeolitic material is a Ti, Ge, Te, Ta, V, Cr, Nb or Zr zeolite of the structure type ABW, ACO, AEI, AEL, AEN, AET, AFG, AFI, AFN, AFO, AFR, AFS, AFT, AFX, AFY, AHT, ANA, APC, APD, AST, ATN, ATO, ATS, ATT, ATV, AWO, AWW, BEA, BIK, BOG, BPH, BRE, CAN, CAS, CFI, CGF, CGS, CHA, CHI, CLO, CON, CZP, DAC, DDR, DFO, DFT, DOH, DON, EAB, EDI, EMT, EPI, ERI, ESV, EUO, FAU, FER, GIS, GME, GOO, HEU, IFR, ISV, ITE, JBW, KFI, LAU, LEV, LIO, LOS, LOV, LTA, LTL, LTN, MAZ, MEI, MEL, MEP, MER, MFI, MFS, MON, MOR, MSO, MTF, MTN, MTT, MTW, MWW, NAT, NES, NON, OFF, OSI, PAR, PAU, PHI, RHO, RON, RSN, RTE, RTH, RUT, SAO, SAT, SBE, SBS, SBT, SFF, SGT, SOD, STF, STI, STT, TER, THO, TON, TSC, VET, VFI, VNI, VSV, WEI, WEN, YUG, ZON and JTO-4 or of a mixed structure comprising two or more of these structures or a mixture of two or more of these zeolites, and the zeolitic material comprises at least one element selected from the group consisting of aluminum, titanium, boron, iron, gallium, vanadium, zirconium, zinc, tin, tellurium, germanium, rare earth metals and a mixture of two or more thereof, and/or at least one element selected from the group consisting of sodium, potassium, magnesium, calcium, metals of groups Ib, IIb and VIIIA and a mixture thereof, as a support material for a catalyst, as a sorbent, as a pigment or as a filler for plastics.

Claims 10-12 (New).--

Exhibit 07-22002

AS ORIGINALLY FILED

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Preparation of a crystalline, zeolitic solid

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The present invention relates to an improved process for the preparation of a crystalline solid, comprising at least one zeolitic material, the reaction discharge from the crystallization being fed, directly and without removal of any  
10 components, to a continuous drying, the solid per se prepared in this manner and its use as a catalyst, as support material for catalysts, as a sorbent, as a pigment or as a filler for plastics, in particular for the preparation of epoxides from olefins, and in turn the preparation of propylene oxide starting from propene with the use of a hydroperoxide, in particular H<sub>2</sub>O<sub>2</sub>.

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Zeolites are known to be crystalline aluminosilicates having ordered channel and cage structures whose pore openings are in the range of micropores smaller than 0.9 nm. The network of such zeolites is composed of SiO<sub>4</sub>- and AlO<sub>4</sub>- tetrahedra which are linked via common oxygen bridges. An overview of the known  
20 structures is to be found, for example, in M.W. Meier, D.H. Olson, Ch. Baerlocher, "Atlas of Zeolite Structure Types", 4th Edition, Elsevier, London 1996, pages 9 to 229.

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Exchangeable cations are present in zeolites in order to compensate the negative electrovalency produced by the incorporation of Al(III) into the Si(IV) silicate lattice; in particular, said cations may be cations of sodium, of potassium, of lithium or of cesium, depending on the preparation process. If these cations are exchanged for protons, for example by an ion exchange, the correspondingly acidic  
30 solids having a zeolite structure, i.e. the H-form, are obtained.

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Zeolites which contain no aluminum and in which some of the Si(IV) has been replaced by titanium as Ti(IV) in the silicate lattice are also known. These titanium zeolites, in particular those having a crystal structure of the MFI type, and possibilities for their preparation are described, for example, in EP-A 0 311 983 or EP-A 405 978. In addition to silicon and titanium, such materials may also contain additional elements, such as, for example, aluminum, zirconium, tin, iron, cobalt, nickel, gallium, boron or small amounts of fluorine. In the zeolite catalysts used in

the novel process, some or all of the titanium of the zeolite may be replaced by vanadium, zirconium, chromium or niobium or a mixture of two or more thereof. The molar ratio of titanium and/or vanadium, zirconium, chromium or niobium to the sum of silicon and titanium and/or vanadium and/or zirconium and/or chromium and/or niobium is as a rule from 0.01 : 1 to 0.1 : 1.

It is known that titanium zeolites can be identified from a specific pattern in the determination of the X-ray diffraction diagrams and additionally from a skeletal vibration band in the infrared range at about 960 cm<sup>-1</sup> and can thus be distinguished from alkali metal titanates or crystalline or amorphous TiO<sub>2</sub> phases.

It is known that titanium zeolites having the MFI structure are suitable as catalysts for oxidation reactions. Thus, for example, EP-A 0 100 118 and EP-A 0 100 119 disclose a process in which propene can be epoxidized in the aqueous phase with hydrogen peroxide over titanium zeolites to give propylene oxide. The preparation of cyclohexanone oxime from cyclohexanone by reaction with ammonia and hydrogen peroxide is described in EP-A 0 208 311. Further reactions used in such catalysts, such as the hydroxylation of aromatics and the oxidation of saturated C<sub>2</sub>-to C<sub>18</sub>-hydrocarbons with H<sub>2</sub>O<sub>2</sub> are disclosed in GB-A 2 116 974 and EP-A 0 376 453, respectively.

Typically, the abovementioned titanium zeolites are prepared by reacting an aqueous mixture of an SiO<sub>2</sub> source, a titanium oxide and a nitrogen-containing organic base, such as, for example, tetrapropylammonium hydroxide, in the presence or absence of an alkali solution in a pressure-resistant container at elevated temperatures for several hours or a few days, a crystalline product being obtained. This is as a rule filtered off, washed and dried and calcined at elevated temperatures to remove the nitrogen-containing organic phase. In the powder thus obtained, at least some of the titanium is present within the zeolite framework in varying proportions with four-, five- or six-fold coordination (Behrens et al., J. Chem. Soc., Chem. Commun. (1991) 678 - 680). In order to improve the catalytic behavior, this may be followed by repeated treatment by washing with a solution of hydrogen peroxide in sulfuric acid, after which the titanium zeolite powder has to be dried and calcined again, as described, for example, in EP-A 0 276 362. The titanium zeolite powder thus obtained must finally be processed with addition of suitable binders in a shaping step in order to make it available as a catalyst in a form capable of being handled. One method for this purpose is described in EP-A 0 200 260.

The above-described crystallization of the titanium zeolite from suitable starting materials by hydrothermal reaction is generally carried out at from 50 to 250°C over a sufficiently long period, an autogenous pressure being established as a function of the temperature.

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After the crystallization, there is the problem of separating the desired crystalline solid, having particle sizes of, as a rule, substantially less than 1 µm, from the strongly alkaline mother liquor still containing organic template. For this purpose, EP-A 0 893 158 describes, in the examples, either the separation by conventional centrifuging and subsequent washing of the solid or the addition of flocculants with subsequent centrifuging. According to this publication, the subsequent drying is carried out by spray-drying or drying by means of fluidized-bed spray granulation. Both the separation of the zeolite from the suspension obtained in the crystallization and the addition of flocculants constitute an additional process step which is time-consuming and expensive.

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It is an object of the present invention to provide a process for the preparation of a crystalline solid comprising at least one zeolitic material, which process does not have the abovementioned disadvantages and in particular manages without additional intermediate steps between crystallization and drying.

20

We have found that this object is achieved by a process for the preparation of a crystalline solid comprising at least one zeolitic material, in which the solid is crystallized from at least one precursor compound and the reaction discharge of the crystallization is fed directly to a drying stage. Here, the term "directly" means that no removal of any components is effected between crystallization and drying, and preferably the product of the crystallization is fed to the drying stage without a further intermediate stage.

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30 The novel drying is preferably effected by means of spray-drying or drying by means of fluidized-bed spray granulation, each of which may be carried out continuously or batchwise. The drying is dried while maintaining a temperature in the range of from 100 to 350°C, preferably from 100 to 250°C, while maintaining the safety conditions necessary in the process, until the free-flowing powder is obtained. The drying is preferably carried out in an atmosphere which comprises oxygen and at least one inert gas. This atmosphere is preferably circulated as a carrier gas stream. Conventional inert gases, such as, for example, nitrogen, carbon

monoxide, carbon dioxide, helium and argon or mixtures of two or more thereof, may be used as the inert gas. The oxygen content of the atmosphere is preferably less than 10, more preferably less than 5, % by volume. Furthermore, a stack gas mixture having a CO<sub>x</sub> content which ensures that there are no explosion problems may be used as inert gas, it being possible to obtain such a stack gas mixture by combustion of natural gas for stack gas production and it being possible simultaneously to generate energy for the energy-intensive stages of the process.

In the drying according to the invention, it is essential that the atmosphere be adjusted, in particular with respect to the oxygen content, so that the procedure is carried out safely outside the explosion limits.

If the crystallization described at the outset is carried out in the presence of a template compound, this template compound which may still be adhering to the crystalline solid as dry material can be removed in a downstream step by means of a preferably aqueous wash solution and can be recycled to the crystallization step. However, the main part of the template is removed during the drying of the reaction discharge, the condensable template compounds then present in the carrier gas stream being condensed out.

20 The present invention thus also relates to an integrated process for the preparation of a crystalline solid comprising at least one zeolitic material, in which

- (i) the solid is continuously crystallized from at least one precursor compound in the presence of at least one template compound,
  - (ii) the reaction discharge from the crystallization is continuously spray-dried, no component of the reaction discharge of the crystallization being separated off before the drying,
  - (iii) the drying is carried out in an atmosphere comprising oxygen, preferably less than 10% by volume of oxygen, and at least one inert gas, this atmosphere being circulated as a carrier gas stream,
  - (iv) template compounds condensable from the carrier gas stream after contact of the stream with the reaction discharge to be dried are condensed out and are recycled to (i),
  - (v) the spray-dried crystalline solid from (ii) is subjected to a continuous wash process in which template compounds which are included in the crystalline solid are separated off and recycled to (i), and
  - (vi) the crystalline solid obtained from (v) is calcined, the energy released as a

result of burning of the remaining amount of template compounds being fed back to (i).

In addition, additives which serve for binding the spray-dried material, i.e. imparting mechanical stability to said material, or for doping the spray-dried material with catalytically active components can of course also be added to the reaction discharge prior to drying, and the application of metals for the use of the resulting solid as an oxidation catalyst according to DE-A 44 25 672 should be mentioned here.

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There are no restrictions at all with regard to the crystalline solids which are dried or prepared by the novel process and comprise at least one zeolitic material. The following zeolites may be mentioned individually.

15

Ti, Ge, Te, Ta, V, Cr, Nb and Zr zeolites and in particular Ti zeolites are preferably used.

20

These include specifically Ti, Ge, Te, Ta, V, Cr, Nb or Zr zeolites of the structure type ABW, ACO, AEI, AEL, AEN, AET, AFG, AFI, AFN, AFO, AFR, AFS, AFT, AFX, AFY, AHT, ANA, APC, APD, AST, ATN, ATO, ATS, ATT, ATV, AWO, AWW, BEA, BIK, BOG, BPH, BRE, CAN, CAS, CFI, CGF, CGS, CHA, CHI, CLO, CON, CZP, DAC, DDR, DFO, DFT, DOH, DON, EAB, EDI, EMT, EPI, ERI, ESV, EUO, FAU, FER, GIS, GME, GOO, HEU, IFR, ISV, ITE, JBW, KFI, LAU, LEV, LIO, LOS, LOV, LTA, LTL, LTN, MAZ, MEI, MEL, MEP, MER, MFI, MFS, MON, MOR, MSO, MTF, MTN, MTT, MTW, MWW, NAT, NES, NON, OFF, OSI, PAR, PAU, PHI, RHO, RON, RSN, RTE, RTH, RUT, SAO, SAT, SBE, SBS, SBT, SFF, SGT, SOD, STF, STI, STT, TER, THO, TON, TSC, VET, VFI, VNI, VSV, WEI, WEN, YUG, ZON and ITQ-4 or of a mixed structure comprising two or more of these structures or a mixture of two or more of these zeolites, where those having the MFI structure, BEA structure, MEL structure, ITQ-4 or MFI/MEL mixed structure in turn are to be regarded as particularly preferred. Zeolites of this type are described, for example, in the abovementioned publication by W.M. Meier et al.

30

Particularly preferred catalysts are specifically the Ti-containing zeolite catalysts, which are generally referred to as "TS-1", "TS-2", "TS-3", "ZSM-48" and "ZSM-12", in each case with Ti, TTM-1, Ti-RUT, Ti-MCM-35, titanium-containing

zeolites of the type "UTD-1", "CIT-5", "CIT-1" and "SSZ-24" and Ti zeolites having a skeletal structure isomorphous with beta-zeolite.

- For example, titanium zeolites as disclosed, for example, in US 3 329 481 are used.
- 5 In the case of such titanium zeolites, some of the Si(IV) originally present in the silicate lattice is replaced by titanium as Ti(IV).

Further titanium zeolites, in particular those having a crystal structure of the MFI type and possibilities for their preparation are described, inter alia, in

10 US 4 410 501, EP-A 0 311 983, US 4 666 692, DE-A 3 047 798 or BE 1 001 038, the content of which in this respect is hereby fully incorporated by reference in the context of the present application. Further titanium-containing zeolites which can be readily used in the present invention and have a structure differing from the MFI structure are described, for example, in EP-A 0 405 978. In addition to silicon

15 and titanium, such zeolites may also contain additional elements, such as aluminium (as described, inter alia, in DE-A 31 41 283), gallium (EP-A 0 266 825), boron (US 4 666 692) or small amounts of fluorine (EP-A 0 292 363). Regarding the zeolites described there, the content of the applications described above is also hereby fully incorporated by reference in the context of the present

20 application.

Further zeolite catalysts which can be used in the process of the present invention are described, inter alia, in US-A 5 430 000 and WO 94/29408, the content of which in this context is hereby incorporated by reference in the present application.

25 Examples of further titanium-containing zeolites are those having the structure of ferrierite or  $\beta$ -zeolite or of mordenite.

Furthermore, the following zeolite catalysts may be used in the novel process:

- 30 Catalysts having a zeolite structure, as are described in DE-A 196 23 611.8, which is hereby fully incorporated by reference, with respect to the catalysts described therein, in the context of the present application.
- 35 These are oxidation catalysts based on titanium silicates or vanadium silicates having a zeolite structure, reference being made to the structures stated above as being preferred with regard to the zeolite structure. These catalysts are

characterized in that they are formed, as described in detail in the above application, by shaping processes which impart strength.

- Furthermore, oxidation catalysts based on titanium silicates or vanadium silicates having a zeolite structure and containing from 0.01 to 30% by weight of one or more noble metals from the group consisting of ruthenium, rhodium, palladium, osmium, iridium, platinum, rhenium, gold and silver, which are likewise characterized in that they have been formed by shaping processes which impart strength, may be used. Such catalysts are described in DE-A 196 23 609.6, which is hereby fully incorporated by reference, with respect to the catalysts described therein, in the context of the present application.

- Regarding the shaping processes which impart strength, the binders and the assistants and the structure of the oxidation catalysts, reference may be made to DE-A 196 23 611.8.

- The oxidation catalyst described in DE-A 196 23 609.6 contains from 0.01 to 30, in particular from 0.05 to 15, especially from 0.1 to 8, % by weight, based in each case on the amount of the titanium or vanadium zeolites, of said noble metals. Here, palladium is particularly preferred. The noble metals can be applied to the catalyst in the form of suitable noble metal components, for example in the form of water-soluble salts, before, during or after the shaping step which imparts strength.

- Furthermore, the following catalysts can be used according to the invention:

- A molding containing at least one porous oxidic material and obtainable by a process which comprises the following stages:
- (I) addition of a mixture containing at least one alcohol and water to a mixture containing a porous oxidic material or a mixture of two or more thereof, and
  - (II) kneading, molding, drying and calcining the mixture added according to stage (I).

- Details of this catalyst are to be found in DE-A 197 23 751.7, which is hereby fully incorporated by reference in the context of the present application.

According to the invention, it is furthermore possible to use silica-containing solids

which can be prepared by a process which comprises the following stage (I):

- (I) bringing at least one precursor of silica into contact with at least one structure former in a liquid medium, characterized in that the structure former is a polyethyleneimine or a mixture of two or more thereof.

5 Details of this solid are to be found in DE-A 197 32 865.2, the context of which in this respect is hereby fully incorporated by reference into the present application.

- 10 Further readily usable catalysts are moldings which comprise an inert support and, applied thereon, at least one silicate, preferably a crystalline silicate, obtainable by applying a mixture containing at least one silicate and at least one metal acid ester or a hydrolysis product thereof or a combination of metal acid ester and hydrolysis product thereof to an inert support, as described in DE-A 197 54 924.1, the content  
15 of this application in this respect likewise being hereby incorporated by reference into the present application.

According to the invention, it is furthermore possible to use moldings comprising at least one silicate and at least one metal oxide, preparable by a process which  
20 comprises the following stage (i):

- (i) mixing of the at least one silicate with at least one metal oxide sol which has a low content of alkali metal and alkaline earth metal ions,
- 25 as described in DE-A 198 15 879.3.

The content of this application in this respect is hereby likewise incorporated by reference in the context of the present application.

- 30 According to the invention, it is furthermore possible to use titanium silicalites having an RUT structure, preparable by a process which comprises the steps (i) and (ii):

- 35 (i) preparation of a mixture of at least one SiO<sub>2</sub> source and at least one titanium source;
- (ii) crystallization of the mixture from (i) in a pressure-resistant container with

addition of at least one template compound, a suspension being obtained, characterized in that amines or ammonium salts which are suitable for stabilizing cages of the silicate structure [445462] and [44566581] are used as the template compound.

5

Details of these catalysts are to be found in DE-A 198 39 792.5.

According to the invention, it is moreover possible to use the silicas described in DE-A 198 47 630.2 having mesopores and micropores, which silicas preferably have one or more of the following features (i) to (iii):

(i) a sum of the specific surface areas of the mesopores and micropores of at least 200 m<sup>2</sup>/g;

15 (ii) a sum of the pore volumes of the mesopores and micropores of at least 0.2 ml/g;

(iii) a maximum of the diameter distribution of the mesopores of at least 3 nm.

20 Further details of these catalysts are to be found in the abovementioned application, the context of which in this respect is hereby fully incorporated by reference into the present application.

As stated at the outset, the zeolite-containing crystalline solids prepared by the novel process can be used in a conventional manner as catalysts, support materials for catalysts, sorbents, as a pigment or as a filler for plastics, the use for the preparation of alkylene oxides starting from alkenes with the use of a hydroperoxide, in particular for the preparation of propylene oxide by reacting propene with H<sub>2</sub>O<sub>2</sub>, being mentioned in particular.

30

The present invention is to be illustrated with reference to an example.

#### EXAMPLE

35 11.98 kg of tetraethoxysilane, 240 g of tetraethyl orthotitanate and a mixture of 7.06 kg of tetrabutylammonium hydroxide (40% by weight in water) in 10.54 kg of demineralized water were mixed in a stirrable steel pressure-resistant container

and homogenized for one hour at room temperature. The alcohol formed was distilled off, the residue was made up to 18.1 kg of water and crystallization was effected in the course of 24 hours at 175°C while stirring.

- 5 The crystallization product was transferred without further separation or purification steps, via a pipeline, into a spray dryer (from Niro) and was sprayed at a rate of 3 l/h via a nozzle. The inlet temperature was 230°C, with an outlet temperature of from 110 to 120°C. The carrier gas used was nitrogen with 2% by volume of oxygen. The amount of drying gas was 70 m<sup>3</sup>(S.T.P.)/h, the drying gas being preheated to 110°C by means of the exit gas.
- 10

The yield of SiO<sub>2</sub> in the titanium zeolite over the integrated steps of the crystallization and spray drying was 94%, based on SiO<sub>2</sub> used.

## FOR FURTHER PROSECUTION IN US

We claim:

- 5      1. A process for the preparation of a crystalline solid comprising at least one zeolitic material, in which the solid is crystallized from at least one precursor compound and the reaction discharge of the crystallization is fed directly to a drying stage, drying being carried out in an atmosphere comprising less than 10% by volume of oxygen and at least one inert gas.
- 10     2. The process as claimed in claim 1, characterized in that said drying is spray-drying.
- 15     3. The process as claimed in claim 1 or 2, characterized in that said crystallization is carried out in the presence of at least one template compound.
- 20     4. The process as claimed in claim 3, characterized in that, after contact with the atmosphere in the form of a carrier gas stream with the reaction discharge to be dried, condensable template compounds present in the stream are condensed out.
- 25     5. The process as claimed in claim 3, characterized in that template compounds which are included in the dried crystalline solid are separated from the solid by means of at least one wash process.
- 30     6. A crystalline solid preparable by a process as claimed in claim 1, characterized in that the zeolitic material is a Ti, Ge, Te, Ta, V, Cr, Nb or Zr zeolite of the structure type ABW, ACO, AEI, AEL, AEN, AET, AFG, AFI, AFN, AFO, AFR, AFS, AFT, AFX, AFY, AHT, ANA, APC, APD, AST, ATN, ATO, ATS, ATT, ATV, AWO, AWW, BEA, BIK, BOG, BPH, BRE, CAN, CAS, CFI, CGF, CGS, CHA, CHI, CLO, CON, CZP, DAC, DDR, DFO, DFT, DOH, DON, EAB, EDI, EMT, EPI, ERI, ESV, EUO, FAU, FER, GIS, GME, GOO, HEU, IFR, ISV, ITE, JBW, KFI, LAU, LEV, LIO, LOS, LOV, LTA, LTL, LTN, MAZ, MEI, MEL, MEP, MER, MFI, MFS, MON, MOR, MSO, MTF, MTN, MTT, MTW, MWW, NAT, NES, NON, OFF, OSI, PAR, PAU, PHI, RHO, RON, RSN, RTE, RTH, RUT, SAO, SAT, SBE, SBS, SBT, SFF, SGT, SOD, STF, STI, STT, TER,

THO, TON, TSC, VET, VFI, VNI, VSV, WEI, WEN, YUG, ZON and ITQ-4 or of a mixed structure comprising two or more of these structures or a mixture of two or more of these zeolites.

- 5      7. A solid as claimed in claim 6, characterized in that the zeolitic material  
comprises at least one element selected from the group consisting of  
aluminum, titanium, boron, iron, gallium, vanadium, zirconium, zinc, tin,  
tellurium, germanium, rare earth metals and a mixture of two or more  
thereof, and/or at least one element selected from the group consisting of  
10     sodium, potassium, magnesium, calcium, metals of groups Ib, IIB and VIIIA  
and a mixture of two or more thereof.
- 15     8. The use of a solid preparable as claimed in claim 1 or of a solid as claimed  
in claim 6 as a catalyst, as a support material for a catalyst, as a sorbent, as  
a pigment or as a filler for plastics.
- 20     9. An integrated process for the preparation of a crystalline solid comprising  
at least one zeolitic material, in which  
(i)    the solid is continuously crystallized from at least one precursor  
compound in the presence of at least one template compound,  
(ii)    the reaction discharge from the crystallization is continuously  
spray-dried, no component of the reaction discharge of the  
crystallization being separated off before the drying,  
(iii)   the drying is carried out in an atmosphere comprising oxygen,  
preferably less than 10% by volume of oxygen, and at least one  
25     inert gas, this atmosphere being circulated as a carrier gas stream,  
(iv)    template compounds condensable from the carrier gas stream after  
contact of the stream with the reaction discharge to be dried are  
condensed out and are recycled to (i),  
30     (v)    the spray-dried crystalline solid from (ii) is subjected to a  
continuous wash process in which template compounds which are  
included in the crystalline solid are separated off and recycled to  
(i), and  
35     (vi)   the crystalline solid obtained from (v) is calcined, the energy  
released as a result of burning of the remaining amount of  
template compounds being fed back to (i).

**Abstract**

Process for the preparation of a crystalline solid comprising at least one zeolitic material, in which the solid is crystallized from at least one precursor compound and the reaction discharge of the crystallization is fed directly to a drying stage.

# *Declaration, Power of Attorney*

Page 1 of 3

0050/050594

We (I), the undersigned inventor(s), hereby declare(s) that:

My residence, post office address and citizenship are as stated below next to my name,

We (I) believe that we are (I am) the original, first, and joint (sole) inventor(s) of the subject matter which is claimed and for which a patent is sought on the invention entitled

## **Preparation of a crystalline, zeolitic solid**

the specification of which

[ ] is attached hereto.

[ ] was filed on \_\_\_\_\_ as

Application Serial No. \_\_\_\_\_

and amended on \_\_\_\_\_.

[x] was filed as PCT international application

Number PCT/EP00/07704

on August 7, 2000

and was amended under PCT Article 19

on \_\_\_\_\_ (if applicable).

We (I) hereby state that we (I) have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

We (I) acknowledge the duty to disclose information known to be material to the patentability of this application as defined in Section 1.56 of Title 37 Code of Federal Regulations.

We (I) hereby claim foreign priority benefits under 35 U.S.C. § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed. Prior Foreign Application(s)

Application No.	Country	Day/Month/Year	Priority Claimed
19939416.4	Germany	20 August 1999	[x] Yes [ ] No

We (I) hereby claim the benefit under Title 35, United States Codes, § 119(e) of any United States provisional application(s) listed below.

(Application Number) \_\_\_\_\_ (Filing Date) \_\_\_\_\_

(Application Number) \_\_\_\_\_ (Filing Date) \_\_\_\_\_

We (I) hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

Application Serial No.	Filing Date	Status (pending, patented, abandoned)
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____

And we (I) hereby appoint:

Norman F. Oblon, Registration Number 24, 618;  
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Stephen G. Baxter, Registration Number 32, 884;  
Richard L. Treanor, Registration Number 36, 379;  
Robert W. Hahl, Registration Number 33, 893, our (my) attorneys, with full

(10) powers of substitution and revocation, to prosecute this application and to transact all business in the Patent Office connected therewith; and we (I) hereby request that all correspondence regarding this application be sent to the firm of **OBLON, SPIVAK, McCLELLAND, MAIER & NEUSTADT, P. C.**, whose Post Office Address is: Fourth Floor, 1755 Jefferson Davis Highway, Arlington, Virginia 22202.

We (I) declare that all statements made herein of our (my) own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

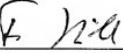
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